

the two isolated isomers, (4) corresponds to the major product and is found to be *cis* at the *BC* junction. The three rings of compound (4) can, in principle, exist in two distinct chair-chair-chair conformations owing to its *cis-anti-cis* stereochemistry. In one of these two conformations, however, the methyl ester at C10 experiences two repulsive interactions with the C14 carbonyl and the C11 methylene. The X-ray diffraction analysis indicates that compound (4) therefore prefers to adopt the chair-chair-chair conformation in which only the methyl at C8 experiences interaction with the carbonyl group at C1. In addition this confirms the *cis* stereochemistry of the *AB* ring junction of the starting compound (3).

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Structure of 7,7-Dimethyldihydropyrnopetrocropane

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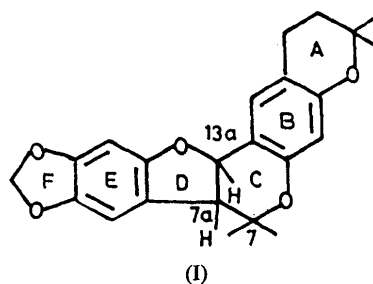
Abstract. 1,2,7a,13a-Tetrahydro-3,3,7,7-tetramethyl-3*H*,7*H*-[1,3]dioxolo[4'',5'':5',6']benzofuro[2',3':4,3]-pyrano[3,2-*g*][1]benzopyran, C₂₃H₂₄O₅, *M_r* = 380.44, monoclinic, *P*2₁/*c*, *a* = 6.403 (3), *b* = 28.081 (5), *c* = 10.807 (4) Å, β = 97.56 (3)°, *V* = 1926.59 Å³, *Z* = 4, *D_x* = 1.311 Mg m⁻³, μ = 0.66 mm⁻¹, *F*(000) = 808, λ(Cu Kα) = 1.5418 Å, *T* = 296 K, final *R* and *wR* are 0.0573 and 0.0699 respectively using 2405 observed reflections. The basic benzofurobenzopyran skeleton has a *cis* ring junction with a staggered conformation viewed from C(7) to C(7a). Intermolecular distances indicate the possibility of C—H...O interactions.

Introduction. A number of structurally related oxygen heterocyclic compounds, isolated from nature, were reported to be biologically active, showing antifungal and antitumor activity (Vanetten, 1976; Kojima, Fukushima, Ueno & Saiki, 1970). The antifungal activity may depend on the molecular geometry (Perrin & Cruickshank, 1969). From two possible conformations of the benzofuro-

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benzopyran skeleton in the *cis* arrangement (I), the most stable is the staggered one (Pachler & Underwood, 1967).



In order to compare the structure of the basic benzofurobenzopyran skeleton of this synthesized compound with the related natural products and to correlate the suggested structure–activity (Perrin & Cruickshank, 1969) relationship, a detailed structure analysis by X-ray diffraction methods was undertaken.

Experimental. The title compound was synthesized by LiPdCl₄-catalyzed Heck arylation of chromene-

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent temperature factors U_{eq} ($\text{\AA}^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	-2247 (3)	1659 (1)	-403 (2)	46 (2)
C(2)	-3343 (3)	2098 (1)	12 (2)	48 (2)
C(3)	-1840 (3)	2515 (1)	310 (2)	36 (2)
O(4)	-189 (2)	2376 (1)	1306 (1)	38 (1)
C(4a)	694 (3)	1937 (1)	1230 (2)	33 (2)
C(5)	2557 (3)	1857 (1)	2029 (2)	35 (2)
C(5a)	3575 (3)	1423 (1)	2005 (2)	33 (2)
O(6)	5481 (2)	1377 (1)	2739 (1)	40 (1)
C(7)	6197 (3)	897 (1)	3080 (2)	38 (2)
C(7a)	6090 (2)	593 (1)	1885 (2)	33 (2)
C(7b)	6314 (2)	71 (1)	2116 (2)	33 (2)
C(8)	8071 (3)	-219 (1)	2460 (2)	39 (2)
C(8a)	7668 (3)	-690 (1)	2636 (2)	39 (2)
O(9)	9095 (2)	-1058 (1)	2943 (2)	53 (2)
C(10)	7869 (4)	-1473 (1)	2891 (5)	85 (5)
O(11)	5720 (2)	-1355 (1)	2749 (2)	49 (2)
C(11a)	5647 (3)	-880 (1)	2509 (2)	36 (2)
C(12)	3883 (3)	-599 (1)	2168 (2)	37 (2)
C(12a)	4296 (2)	-131 (1)	1965 (2)	34 (2)
O(13)	2767 (2)	200 (1)	1578 (2)	39 (1)
C(13a)	3901 (3)	604 (1)	1122 (2)	35 (2)
C(13b)	2728 (3)	1058 (1)	1213 (2)	33 (2)
C(14)	855 (3)	1148 (1)	446 (2)	36 (2)
C(14a)	-205 (3)	1576 (1)	443 (2)	36 (2)
C(15)	-2960 (4)	2925 (1)	853 (2)	49 (2)
C(16)	-786 (4)	2672 (1)	-796 (2)	53 (3)
C(17)	4850 (4)	710 (1)	4036 (2)	48 (2)
C(18)	8481 (3)	964 (1)	3653 (3)	54 (3)

(6,7-dihydro-2,2,8,8-tetramethyl-2*H*,8*H*-benzo[1,2-*b*:5,4-*b'*]dipyran) with 2-chloromercurio-4,5-methylene-dioxyphenol. The intermediate diromene was obtained from resorcinol through a series of steps (Narkhede, 1990). The compound was crystallized using a mixture of petroleum ether and benzene as solvent.

A colourless crystal of dimensions $0.25 \times 0.20 \times 0.35$ mm was used for intensity-data collection using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å), $\omega/2\theta$ scan. The cell dimensions were refined using 25 reflections in the range $30 \leq \theta \leq 47^\circ$. Two standard reflections (397 and 2,20,5), measured every 1800 s, showed no significant intensity variation. A total of 3373 unique reflections were measured, in the range $2 \leq \theta \leq 70^\circ$; $0 \leq h \leq 7$, $0 \leq k \leq 34$, $-13 \leq l \leq 13$. *Lp* corrections were applied, but no absorption or extinction corrections. The structure was solved by direct methods using *MULTAN*84 (Main, Germain & Woolfson, 1984), taking 2635 observed reflections with $F_o \geq 2\sigma|F_o|$. Most of the non-H atoms were assigned from the first *E* map and the rest were located by Fourier recycling using *SHELX*76 (Sheldrick, 1976). All H atoms were located from the difference Fourier maps. All non-H atoms refined with anisotropic thermal parameters and H atoms (except H102 which was unstable on refinement and was held fixed) with isotropic thermal

Table 2. Bond distances (Å) and angles ($^\circ$) with e.s.d.'s in parentheses

C(2)—C(1)	1.517 (3)	C(13a)—C(7a)	1.530 (2)
C(14a)—C(1)	1.511 (2)	C(8)—C(7b)	1.399 (3)
C(3)—C(2)	1.522 (3)	C(12a)—C(7b)	1.401 (2)
O(4)—C(3)	1.459 (2)	C(8a)—C(8)	1.364 (3)
C(15)—C(3)	1.515 (3)	O(9)—C(8a)	1.391 (2)
C(16)—C(3)	1.514 (3)	C(11a)—C(8a)	1.390 (2)
C(4a)—O(4)	1.366 (2)	C(10)—O(9)	1.402 (3)
C(5)—C(4a)	1.396 (2)	O(11)—C(10)	1.405 (3)
C(14a)—C(4a)	1.396 (3)	C(11a)—O(11)	1.359 (3)
C(5a)—C(5)	1.384 (3)	C(12)—C(11a)	1.387 (3)
O(6)—C(5a)	1.371 (2)	C(12a)—C(12)	1.364 (3)
C(13b)—C(5a)	1.397 (3)	O(13)—C(12a)	1.374 (2)
C(7)—O(6)	1.456 (3)	C(13a)—O(13)	1.468 (2)
C(7a)—C(7)	1.541 (3)	C(13b)—C(13a)	1.489 (2)
C(17)—C(7)	1.524 (3)	C(14)—C(13b)	1.389 (3)
C(18)—C(7)	1.523 (2)	C(14a)—C(14)	1.382 (3)
C(7b)—C(7a)	1.492 (3)		

C(14a)—C(1)—C(2)	110.1 (2)	C(12a)—C(7b)—C(7a)	108.1 (2)
C(3)—C(2)—C(1)	112.5 (2)	C(12a)—C(7b)—C(8)	119.5 (2)
O(4)—C(3)—C(2)	109.2 (2)	C(8a)—C(8)—C(7b)	116.2 (3)
C(15)—C(3)—C(2)	110.3 (2)	O(9)—C(8a)—C(8)	128.6 (2)
C(15)—C(3)—O(4)	104.5 (2)	C(11a)—C(8a)—C(8)	123.2 (2)
C(16)—C(3)—C(2)	113.1 (2)	C(11a)—C(8a)—O(9)	108.2 (2)
C(16)—C(3)—O(4)	107.8 (2)	C(10)—O(9)—C(8a)	105.2 (2)
C(16)—C(3)—C(15)	111.5 (2)	O(11)—C(10)—O(9)	110.1 (2)
C(4a)—O(4)—C(3)	117.5 (2)	C(11a)—O(11)—C(10)	105.2 (2)
C(5)—C(4a)—O(4)	115.7 (2)	O(11)—C(11a)—C(8a)	110.5 (2)
C(14a)—C(4a)—O(4)	123.5 (2)	C(12)—C(11a)—C(8a)	121.6 (2)
C(14a)—C(4a)—C(5)	120.7 (2)	C(12)—C(11a)—O(11)	127.9 (2)
C(5a)—C(5)—C(4a)	119.7 (2)	C(12a)—C(12)—C(11a)	115.0 (2)
O(6)—C(5a)—C(5)	117.2 (2)	C(12)—C(12a)—C(7b)	124.5 (2)
C(13b)—C(5a)—C(5)	120.7 (2)	O(13)—C(12a)—C(7b)	111.8 (2)
C(13b)—C(5a)—O(6)	122.0 (2)	O(13)—C(12a)—C(12)	123.7 (2)
C(7)—O(6)—C(5a)	117.4 (1)	C(13a)—O(13)—C(12a)	105.1 (1)
C(7a)—C(7)—O(6)	108.8 (2)	O(13)—C(13a)—C(7a)	105.2 (1)
C(17)—C(7)—O(6)	107.7 (2)	C(13b)—C(13a)—C(7a)	114.6 (2)
C(17)—C(7)—C(7a)	114.3 (2)	C(13b)—C(13a)—O(13)	111.3 (1)
C(18)—C(7)—O(6)	104.0 (2)	C(13a)—C(13b)—C(5a)	120.6 (2)
C(18)—C(7)—C(7a)	110.1 (2)	C(14)—C(13b)—C(5a)	117.9 (2)
C(18)—C(7)—C(17)	111.5 (2)	C(14)—C(13b)—C(13a)	121.2 (2)
C(7b)—C(7a)—C(7)	114.3 (2)	C(14a)—C(14)—C(13b)	123.0 (2)
C(13a)—C(7a)—C(7)	112.2 (1)	C(4a)—C(14a)—C(1)	120.8 (2)
C(13a)—C(7a)—C(7b)	99.9 (1)	C(14)—C(14a)—C(1)	121.4 (2)
C(8)—C(7b)—C(7a)	132.4 (2)	C(14)—C(14a)—C(4a)	117.8 (2)

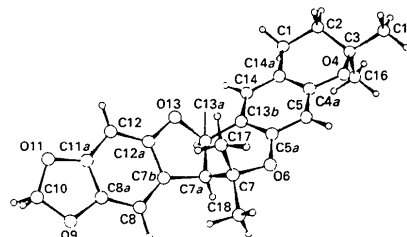


Fig. 1. PLUTO drawing of the molecule.

parameters by least-squares methods based on *F* values, using *SHELX*76. In final refinements, 345 parameters were refined using 2405 reflections with $|F_o| \geq 5\sigma|F_o|$ [neglecting those for which $F_o < F_c$ and $\Delta F/\sigma(F_o) > 4.0$], $R = 0.0573$, $wR = 0.0699$ {where $w = k/[\sigma^2(F) + g(F^2)]$, with $k = 1.000$ and $g = 0.007273$ }. In final difference map $(\Delta\rho)_{\max} = 0.217$, $(\Delta\rho)_{\min} = -0.239$ e Å⁻³, $(\Delta/\sigma)_{\max} = -0.08$. A CYBER-180/840 was used for all the computa-

tions. Atomic scattering factors were those in *SHELX76*.

Discussion. The positional parameters and equivalent temperature factors for non-H atoms are tabulated in Table 1* and bond lengths and angles in Table 2. Fig. 1. represents the *PLUTO*78 (Motherwell & Clegg, 1978) diagram of the molecule.

The molecular skeleton consists of six rings fused together. The benzofurobenzopyran units are *cis* fused [C(7a) and C(13a)] and on viewing from C(7) to C7(a), the conformation is staggered, with torsion angle O(6)—C(7)—C(7a)—C(13a) 54.2 (2)°, which agrees with that obtained from ¹H NMR (Pachler & Underwood, 1967) as the most stable conformation. Ring *D* has an envelope shape with C(13a) 0.473 (2) Å out of the plane passing through the remaining four atoms [with maximum deviation 0.020 (2) Å from the mean plane]. The bond angles C(7a)—C(7b)—C(8) and C(13a)—C(7a)—C(7b), 132.4 (2) and 99.9 (1)° respectively, demonstrate the presence of strain in ring *D*. Ring *C* has an approximate sofa conformation (Livingstone, 1981), and C(7) (to which the methyl groups are attached) is 0.623 (2) Å below the plane passing through the remaining five atoms with maximum deviation 0.037 (2) Å out of the mean plane. The angle between the mean planes passing through rings *C* and *D* is 40.1 (3)°. Unlike ring *C*, the pyran ring *A* is a distorted half chair, and C(3) and O(4) are respectively 0.768 (2) and 0.287 (2) Å out of the least-squares plane through the remaining four atoms. Both the aromatic rings (*B* and *E*) are planar and mutually inclined at an angle 42.0 (3)° satisfying the condition for antifungal activity (Perrin & Cruickshank, 1969). The five-membered dioxolo ring (*F*) has an envelope shape with C(10) deviating by

* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52899 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

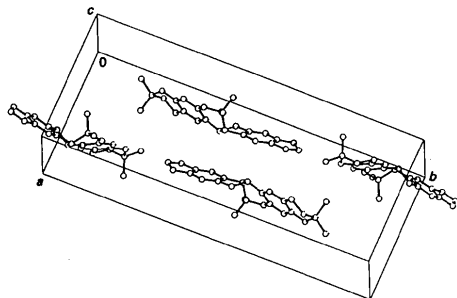


Fig. 2. Packing of the molecules.

Table 3. *Important intermolecular distances (Å) and angles (°)*

	C...O'	H...O'	C—H...O' Angle	Symmetry of O'
C15—H151...O11'	3.193 (4)	2.84 (4)	102 (1)	-x, 1/2 + y, 1/2 - z
C15—H153...O11'	3.193 (4)	2.95 (5)	100 (2)	
C16—H161...O4'	3.208 (4)	2.77 (4)	106 (2)	
C16—H163...O4'	3.208 (4)	2.94 (6)	99 (2)	x, 1/2 - y, -1/2 + z
C8—H8...O13'	3.477 (3)	2.49 (3)	150 (2)	
C12—H121...O9'	3.527 (4)	2.57 (4)	171 (2)	1 + x, y, z
				-1 + x, y, z

0.134 (5) Å from the mean plane passing through the remaining four atoms, which are planar within ± 0.006 (2) Å. In ring *F*, the C(sp³)—O bond lengths [average 1.404 (3) Å] are shorter than the corresponding reported lengths, in the range 1.421 (7) to 1.440 (6) Å for oxolinic acid and its derivatives (Cygler & Huber, 1985; Czugler, Argay, Frank, Meszaros, Kutschabsky & Reck, 1976). In the rest of the molecule, the average C(sp³)—O bond length is 1.461 (2) Å. The average C—O—C bond angles are 105.2 (2) and 117.5 (2)° in five-membered and six-membered rings respectively. The C(sp³)—C(sp³) bond distance ranges from 1.489 (2) to 1.541 (3) Å with a mean value 1.516 (3) Å.

The molecules are stacked almost perpendicular to crystallographic *a* axis (Fig. 2). The intermolecular distances listed in Table 3 are comparatively short, probably due to C—H...O interactions (Taylor & Kennard, 1982).

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